Observation of nanostructured cluster formation of Tm ions in CaF$_2$ crystals

G. Dražić$^a$, S. Kobe$^a$, A.C. Cefalas$^{b,*}$, E. Sarantopoulou$^b$, Z. Kolli$^b$

$^a$ Jozef Stefan Institute, Jamova 39, SI-1000 Ljubljana, Slovenia
$^b$ National Hellenic Research Foundation, TPCI, 48 Vassileos Constantinou Avenue, Athens 11635, Greece

1. Introduction

For high image quality at shorter light wavelengths, defect free optical materials at nanoscale dimensions must be used. For example, lithography at 193 and 157 nm [1], besides posing problems of optical compactness, also places severe restrictions on the refractive index homogeneity of the optical elements (better than 10$^{-7}$), which in turn depends on crystal purity and spatial homogeneity.

Calcium fluoride (CaF$_2$) is considered to be the best optical material for short wavelength applications, and the growth of high-purity CaF$_2$ optical elements is essential not only for industrial but for space applications. Also, high purity wide bandgap fluoride dielectric crystals doped with trivalent rare-earth ions (RE) have been used as passive or active optical elements [2], such as optical filters in the vacuum ultraviolet (VUV) region of the spectrum, X and γ ray scintillators, and VUV emitters. All these optical properties are based on the interconfigurational 4f$^n$ ↔ 4f$^{n-1}$5d strong, dipole allowed transitions. The homogeneity of the concentration of the RE ions determine the refractive index variation, and therefore set the limits of the optical performance of these materials. Thus, the efficiency of optical systems depends on several factors: the structure of the levels of the 4f$^{n-1}$5d electronic configuration of the RE ions [3,4], the homogeneous distribution of the RE ion concentration inside the crystal volume [5,6], and the possible agglomeration of the RE ions at the ionic sites of the host matrix, because the RE ion clustering have an effect on the refractive index of the material [7].

Several analytical techniques based on transmission electron microscopy (TEM) have been used in materials science to study the structure and chemistry of single crystals at atomic resolutions. The local structure is analyzed by high-resolution TEM (HRTEM) imaging, where various parameters such as defocus, thickness of the specimen, and aberrations are examined in the simulated images and compared with experimental results. Similarly, high-resolution scanning-transmission electron microscopy (STEM) and high-resolution high-angle annular dark-field detectors (HAADF–STEM) (Z-contrast methods) allow compositional structures to be resolved with atomic resolution [8].

Up until now, HRTEM has been used to study single crystal CaF$_2$ processed surfaces [9], the structure of CaF$_2$ films and interfaces [10], the formation of RE doped and undoped CaF$_2$ nanoparticles [11,12], and radiation-induced damages [13].

In this communication, we used HRTEM and HAADF–STEM, together with energy dispersive X-ray spectroscopy (EDXS), to investigate the homogeneity of the spatial distribution of Tm$^{3+}$ ions in CaF$_2$ crystals grown from melts using the Bridgman–Stockbarger method. It was found that with a 2-nm electron beam, the concentration of Tm$^{3+}$ ions was inhomogeneously distributed in the crystal bulk in the range of 2.6–6 nm and the ions occupied the host sites of the crystal as 3–5 atom agglomerations. The inhomogeneous Tm$^{3+}$ concentration originates from the local electrostatic field at the ionic sites. From the analysis of the experimental data, it was found that the thickness of the phase transition layer was 0.1 nm.
2. Experimental study

The experimental apparatus for crystal growth has been described in detail previously [2]. CaF₂:Tm³⁺ crystals were grown from liquid melts in carbon crucibles. The concentration of the Tm³⁺ ions in the doped crystals varied from 1.0% to 0.01%.

A JEOL2010F STEM/TEM analytical electron microscope operating at 200 keV was used for HAADF and high-resolution electron microscopy (HREM) imaging. The microscope was equipped with an EDXS detector. A series of quantitative EDXS measurements were performed using beam diameters ranging from 2 to 50 nm to determine the chemical composition of the samples.

Samples for the TEM investigation could not be prepared from bulk, since the monocrystal was very prone to cleaving during the preparation. The crystals were therefore crushed in a mortar, and the resulting powder was subsequently embedded in phenol-formaldehyde resin. Phenol-formaldehyde powder (3–5 wt.%) was added to the CaF₂:Tm³⁺ powder and thoroughly mixed. The mixture was placed in a dye with a suitable diameter, subjected to a pressure ranging from 0.5 to 1 MPa, and cured at 180 °C for few minutes. The resulting pellet was mechanically strong, and there was no difficulty with the subsequent grinding, dimpling, and ion erosion. Due to the high number of powder particles, liquid nitrogen cooling during the ion erosion process was unnecessary, and no charging effects were observed in the TEM.

3. Results and discussion

When the electron beam diameter in the EDXS analysis was larger than the cluster size, the relative standard deviation (R.S.D.) of the Tm ion concentration was dependent only on instrumental factors such as the sensitivity of the counting rate. With long sampling periods, appropriate counting rates, and corrections for the absorption of the electron beam from the sample, the R.S.D. at different points was as low as 5–10%. However, when the electron beam diameter was comparable to the cluster size, or when the average distance between different clusters was larger than the beam size, the repeatability of the measurements was poor and the R.S.D. was inversely proportional to the beam diameter.

Furthermore, the 200-keV electron-beam’s broadening for a 30-nm thick CaF₂ matrix was calculated to be 0.8 nm, and for a 50 nm sample thickness was 1.8 nm. The measurements were performed for sample thicknesses between 30 and 50 nm.

The concentration (%) of the Tm³⁺ ions at different points, using 50 and 2 nm electron beams, is shown in Figs. 1 and 2, respectively. The R.S.D. is higher for the narrower beam (Fig. 2). The experimental and theoretical values of the R.S.D. of the Tm³⁺ concentration for 2, 5, 20, and 50 nm electron beams, respectively, are tabulated in Table 1. The spread of the experimental values of the Tm ion concentrations was higher for narrower beam diameters. The spread between the minimum and maximum concentration of Tm ions, obtained using a 2-nm beam, was 0.5–1.5 wt.% (the stochiometric Tm concentration was 1 wt.%).

There is a large deviation between the theoretical and experimental values in the case of small beam diameters (Table 1). This is attributed to the non-uniform distribution of Tm ions in the form of clusters rather than ions, at beam sizes smaller than 2 nm. Inspection of the areas where analyses were performed showed no damage, down to beam sizes less than 1 nm.

Besides using an EDXS analysis, the appearance of Tm clustering in CaF₂ matrices is verified with HRTEM imaging, which in these experiments provides structural information with a spatial resolution better than 0.2 nm. In most crystalline inorganic materials, including ceramics, semiconductors, and metals, the positions of individual atomic columns can be resolved, at least for the low-index zones. When recorded under optimum conditions, electron micrographs can be directly interpreted in terms of projected crystal potentials. In other cases, simulated images are matched to the experimental imaging features.

HRTEM imaging of CaF₂:Tm³⁺ crystals was performed at different orientations, with different defocus amounts for the electron beam, and with different foil thicknesses. The experimentally obtained images were compared with the simulated images of pure CaF₂ matrices and doped CaF₂ with Tm³⁺ clusters. The simulated images were generated using the “EMS software package”, which allows for modelling and a comparison with experimental images [14]. A through-focus series of simulated images for pure CaF₂ for the [1 1 0] zone is shown in Fig. 3, for 10 nm foil thickness, 21 nm aperture diameter, 8 nm spread of focus, 0.48 cs, and 0.5 mrad beam semi-convergence. The image simulation when one or more columns of Ca atoms were substituted with Tm atoms is shown in Fig. 4. The corresponding crystal structure for this case is shown in Fig. 5. For those calculations, no charge compensation (such as anion vacancies) was taken into consideration. The effect of column substitution by Tm ions on the simulated image is clearly seen in a comparison of Figs. 3 and 4.

The CaF₂:Tm³⁺ HRTEM images were recorded at different areas with non-uniform contrast. A typical image recorded with 10 nm foil thickness and 20 nm defocus is shown in Fig. 6. The foil thickness for EDXS measurements was estimated using the convergent beam diameter.

Table 1

<table>
<thead>
<tr>
<th>Beam diameter (nm)</th>
<th>Measured R.S.D. (%)</th>
<th>Theoretical R.S.D. (%)</th>
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<tr>
<td>2</td>
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<td>50</td>
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Fig. 1. Tm³⁺ concentration at various points using the EDXS technique with 50 nm beam diameter.

Fig. 2. Tm³⁺ concentration at various points using the EDXS technique with 2 nm beam diameter.
beam electron diffraction (CBED) technique, proposed by Kelly et al. [15] and for HRTEM experiments it was estimated from the geometry of the thinned sample (distance from the hole and ion-erosion angle). The variation of the brightness of the brighter dots in the experimental image is similar to the individual image fluctuations of Fig. 4 (for a 20-nm defocused beam). It is evident therefore from the HRTEM images that Tm clustering is taking place in the CaF₂ matrices in agreement with the EDXS analysis.

Furthermore, the STEM–HAADF method was also used to investigate Tm clustering in CaF₂:Tm³⁺ samples (Z-contrast). The STEM–HAADF signal was due to the interaction between the incoming electrons and the atomic nuclei, and the contrast of the image is based on differences in the atomic number (Z). In this case, the contrast of the simulated images depends on many parameters, such as the zone, the thickness, the position, and the concentration of the substituted atoms. Fig. 7 shows the simulated STEM–HAADF image for CaF₂ in the [1 1 0] zone, using a computer simulation code [16], where five columns of Ca atoms were substituted with Tm atoms (seen as bright spots). The Tm ions have a higher Z-value than the Ca and F ions; thus, they are expected to be expressed differently than Ca and F. suitcases where the Tm agglomeration is large enough should be easily identifiable from the brighter contrast on the atomic resolution image of the crystal sample.

Fig. 8 shows the FFT filtered experimental high-resolution image of the CaF₂: Tm³⁺ (1% Tm³⁺) sample in the [1 1 0] zone. Columns with a higher contrast can be clearly seen. By examining several pictures, it was estimated that approximately 10% of the columns have higher contrast. The ratio of the intensity of brighter columns to normal columns was estimated to be around 1.4.

The distribution of brighter columns (enriched in Tm) is relatively non-uniform, as can be seen in Fig. 9. In this figure, a different area of the sample is shown and brighter columns are designated with stars. The radius of the electron beam in the EDXS analysis is also shown. It is estimated that during the EDXS analysis with a 2 nm beam size (the CaF₂ monocrystal was not in a low-index zone), the maximum of 5–10 Tm columns were irradiated. The distribution of the enhanced concentration Tm columns matches quite well with the R.S.D. of the Tm concentration from the EDXS analyses. Therefore, Tm is forming large clusters that are a few tenths of a nanometer, consisted of 3–5 atoms.

These results are in agreement with previous measurements taken from the broad optical spectra of RE ions in host matrices [6]. The degree of the inhomogeneous distribution of the Tm ions, and the clustering in the host crystal, depends on the heat flow gradients across the interfacial layer between the melt and the solid phase, and also on the temperature gradient and stability in the crucible and the spatial correlation of density fluctuations in the liquid phase at the interface. The later is determined by the extend of the local electrostatic field. In a horizontal layer of fluid in which a perpendicular temperature gradient is maintained, its density will be different across the gradient due to the stressing of the interface and hence there will be a tendency for the fluid to establish its density equilibrium, compensating for the defect of the configuration. This tendency will be inhibited by the fluid viscosity. The principal
facts are that when a temperature gradient is established, the fluid becomes unstable. When it eventually relaxes, some parts of the fluid at the interface have zero velocity, which is developed from the dynamic evolution of the system, and therefore they have different ionic density than the moving parts of the fluid. What actually happens at the onset of an instability is that the points of zero velocity resolve themselves into a number of cell patterns, which were solidified during the transition from the liquid to the solid phase. The general theory [17] indicates that the instability is specified by the numerical value of the non-dimensional Rayleigh number

$$R = \frac{g\alpha\beta}{k\nu}$$  

(1)

where $g$ is the acceleration of gravity, $d$ is the thickness of the layer where the temperature gradient is developed, $\beta$ is the adverse uniform temperature gradient, and $\alpha$, $\kappa$ and $\nu$ are the coefficients of volume expansion, thermometric conductivity, and kinematic viscosity, respectively, with approximate values $\alpha \sim 10^{-4} \text{K}^{-1}$, $\kappa \sim 10^{-5} \text{m}^2 \text{s}^{-1}$ and $\nu \sim 10^{-7} \text{m}^2 \text{s}^{-1}$. The uniform temperature gradient in the crucible is in the order of $\beta \sim 10^3 \text{K} \text{m}^{-1}$.

The instability (and thus the patterns of ionic concentration of zero velocity) is maintained and transferred to the solid phase when $R$ exceeds a certain critical value $R_c$. The value of $R_c$ depends on the boundary conditions, and in the case of two free boundaries, $R_c = 657.7$, regardless of the thickness of the layer where the temperature gradient is maintained [17]. Therefore, under the crystal growth conditions with the Bridgman–Stockbarger method, instabilities from the heat flow develop across the phase transition layer (zone), causing fluctuations in the local concentration of ions in the liquid phase and preventing structural homogeneity and single ion substitution. The concentration and density fluctuations are characterized by the wavelength

$$\lambda = 2^{3/2}d$$  

(2)

In the case of melting and crystallization across the interfacial zone, the phase transition from liquid to solid takes place within a thin 1–2 mm temperature gradient zone [18] and this situation allows the Rayleigh number $R$ to exceed the critical value $R_c$. In addition the range of spatial density fluctuations $< (r^2) >$ will be determined by the spatial correlation function of the electrostatic potential $U(r_{ij})$. The electrostatic energy $w(r_{ij})$ between the ionic site (j) with the effective charge $Q_j^\ast$ and all the neighboring $i$ it ionic centers $Q_i^\ast$ is given by

$$w(r) = \sum_i \frac{Q_i^\ast Q_j^\ast}{r_{ij}}$$  

(3)
Finally,

$$< r^{2}_{ij} > = \int_{-\infty}^{\infty} r^{2} \exp \left( - \frac{w(r)}{kT} \right) \, dr$$

(4)

Taking into consideration that

$$w(r) = \sum_{n} Q_{n}^{*} Q_{n}^* \left[ A_{n} r^{l} + B_{n} r^{-(l+1)} \right] P_{l}(\cos \theta) \exp(i m \phi)$$

(5)

Therefore two random points of different ionic concentration will be separated by the correlation distance of the ionic potential $$< r^{2}_{ij} >$$, which depends on the local symmetry as it is expected by Eq. (6) exactly indicated in Fig. 2, where the points with different concentration of Tm ions are separated by 2.6–6 nm. Large concentration fluctuations are expected to appear at the points of intersection of locus of points of zero velocity, Eqs. (1) and (2) and the areas as they are specified by Eq. (4). Furthermore, the pattern of Fig. 9 and Eq. (2) suggest that the phase transition is taking place within a thin layer of \( \sim 0.1 \) nm in the interfacial zone.
4. Conclusion

Using high-resolution analytical methods, it was found that the Tm ion concentration in CaF$_2$ host matrices is inhomogeneous spatially distributed within 2.6 to 6 nm and forms agglomerations of 3–5 ions due to the ionic density fluctuation caused from the electrostatic potential in the crystal. The phase transition from the solid to liquid phase is taking place within a 0.1 nm thick layer in the graphite crucible.

References